

CLAIMS

What is claimed:

1. A process for the preparation of a supported metallocene catalyst comprising:

(a) providing a particulate catalyst support material comprising silica particles impregnated with an alumoxane co-catalyst with at least one-half of said co-catalyst disposed within the internal pore volume of said silica particles;

5 (b) providing a dispersion in an aromatic hydrocarbon solvent of a stereospecific metallocene incorporating a metallocene ligand structure having two sterically dissimilar cyclopentadienyl ring structures coordinated with a central transition metal atom; at least one of said cyclopentadienyl ring structures being a substituted cyclopentadienyl group which provides an orientation with respect to said transition metal atom which is sterically different from the orientation of the other cyclopentadienyl group with respect to said transition metal atom, and both of said cyclopentadienyl groups being in a relationship with each other providing a stereorigid relationship relative to said coordinating transition metal atom to prevent rotation of said ring structures;

10 (c) mixing said metallocene-solvent dispersion and said alumoxane-impregnated silica particles at a temperature of about 10°C or less for a period sufficient to enable said metallocene to become reactively supported on and impregnated within said alumoxane-impregnated silica particles and form a silica-supported catalyst;

(d) recovering said supported catalyst from said aromatic solvent;

15 (e) washing said supported catalyst with a paraffinic hydrocarbon solvent at a
20 temperature of about 10°C or less; and

(f) dispersing said washed catalyst in a viscous mineral oil having a viscosity greater than the viscosity of said paraffinic hydrocarbon solvent.

2. The process of claim 1 wherein the washed catalyst at the time of dispersion in said viscous mineral oil contains a residual amount of said paraffinic hydrocarbon solvent.

3. The process of claim 2 wherein the washing of said supported catalyst with said paraffinic hydrocarbon solvent is effective to reduce the residual aromatic solvent on said supported catalyst to a value of no more than 50 wt.% of said supported catalyst.

4. The process of claim 1 wherein said viscous mineral oil has a viscosity of at least 10 centistokes.

5. The method of claim 4 wherein said paraffinic hydrocarbon solvent has a viscosity of no more than 2 centistokes.

6. The process of claim 1 wherein subsequent to step (d) and prior to step (e) washing the recovered supported metallocene catalyst with an aromatic solvent to remove unsupported metallocene from said supported metallocene catalyst and thereafter washing said supported catalyst in accordance with step (e).

7. The process of claim 1 wherein said silica support material comprises spheroidal

silica particles having an average particle size within the range of 20-60 microns.

8. The process of claim 7 wherein said spheroidal silica particles have an average effective pore diameter within the range of 200-400 Angstroms.

9. The process of claim 8 wherein the weight ratio of said alumoxane to said silica in subparagraph (a) of claim 1 is within the range of about 0.6-2.0.

10. The process of claim 1 wherein said stereospecific metallocene is a syndiospecific metallocene characterized by the formula:



wherein Cp_a is a substituted cyclopentadienyl ring, Cp_b is an unsubstituted or substituted cyclopentadienyl ring; each R is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; each R'_m is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the cyclopentadienyl rings imparting stereorigidity to the metallocene and is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal from the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; $0 \leq p \leq 3$; $0 \leq m \leq 4$; $1 \leq n \leq 4$; and wherein R'_m is selected such that $(Cp_bR'_m)$ is a sterically different ring than (Cp_aR_n) .

11. The process of claim 10 wherein R is selected such that (Cp_aR_n) forms a substituted or unsubstituted fluorenyl group.

12. The process of claim 11 wherein Me is titanium, zirconium, hafnium, or vanadium.

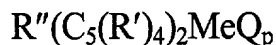
13. The process of claim 12 wherein R" is a methylene, ethylene, organosilyl, substituted methylene, or substituted ethylene radical.

14. The process of claim 13 wherein R is selected such that (Cp_aR_n) forms a substituted or unsubstituted fluorenyl radical having bilateral symmetry and R' is selected such that $(Cp_bR'_m)$ forms an alkyl substituted or unsubstituted cyclopentadienyl radical having bilateral symmetry.

15. The process of claim 14 wherein $R''(Cp_aR_n)(Cp_bR'_m)$ forms an isopropylidene(cyclopentadienyl-1-2,7-di-tert-butyl fluorenyl) ligand or a diphenyl methylene(cyclopentadienyl-1-fluorenyl) ligand.

16. The process of claim 10 wherein said stereospecific metallocene is selected from the group consisting of isopropylidene(cyclopentadienyl-1-2,7-di-tert-butyl fluorenyl) zirconium dichloride and diphenyl methylene(cyclopentadienyl-1-fluorenyl) zirconium dichloride and mixtures thereof.

17. The process of claim 1 wherein said stereospecific metallocene is an isospecific metallocene characterized by the formula:



wherein each $(C_5(R')_4)$ is a substituted cyclopentadienyl ring; each R' is the same or different and is
5 a hydrogen or hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the two $(C_5(R')_4)$ rings imparting stereorigidity to said metallocene with the two $(C_5(R')_4)$ rings being in a racemic configuration relative to Me, and R'' is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an
10 aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal as designated in the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; and $0 \leq p \leq 3$.

18. The method of claim 17 wherein said $(C_5(R')_4)$ groups are indenyl groups which are substituted or unsubstituted.

19. The method of claim 18 wherein said indenyl groups are each substituted at the proximal position.

20. The method of claim 18 wherein Me is titanium, zirconium, hafnium, or vanadium.

21. The method of claim 20 wherein R" is a methylene, ethylene, organosilyl, substituted methylene, or substituted ethylene radical.

22. The method of claim 21 wherein said isospecific metallocene is selected from the group consisting of racemic dimethylsilyl(2-methyl-4-phenyl indenyl)₂ zirconium dichloride, racemic dimethylsilyl(2-methyl-4-indenyl)₂ zirconium dichloride, and racemic dimethylsilyl(2-methyl-4,5-benzo indenyl)₂ zirconium dichloride and admixture thereof.

23. A process for the preparation of a supported metallocene catalyst comprising:

(a) providing a particulate catalyst support material comprising spheroidal silica particles having an average particle size within the range of 20-60 microns and an average effective pore diameter within the range of 200-400 Angstroms;

5 (b) contacting said particulate support material with an alumoxane co-catalyst in an aromatic carrier liquid;

(c) heating said mixture of support, carrier liquid, and alumoxane co-catalyst at an elevated temperature for a period sufficient to fix said alumoxane on said particulate support material with at least one-half of said co-catalyst disposed within the internal pore volume of said silica particles;

10 (d) cooling said mixture and separating said alumoxane-containing support material from said carrier liquid;

(e) washing said alumoxane containing support material with an aromatic solvent to remove excess alumoxane therefrom;

15 (f) cooling said alumoxane containing support material to a reduced temperature of about 10°C or less and at said reduced temperature adding to said support material a dispersion in an aromatic hydrocarbon solvent of a stereospecific metallocene incorporating a metallocene ligand structure having two sterically dissimilar cyclopentadienyl ring structures coordinated with a central transition metal atom; at least one of said cyclopentadienyl ring structures being a substituted cyclopentadienyl group which provides an orientation with respect to
20 said transition metal atom which is sterically different from the orientation of the other cyclopentadienyl group with respect to said transition metal atom, and both of said cyclopentadienyl

groups being in a relationship with each other providing a stereorigid relationship relative to said coordinating transition metal atom to prevent rotation of said ring structures;

25 (g) mixing said metallocene-solvent dispersion and said alumoxane-impregnated silica particles at a temperature of about 10°C or less for a period sufficient to enable said metallocene to become reactively supported on and impregnated within said alumoxane-impregnated silica particles and form a silica-supported catalyst;

 (h) recovering the resulting supported metallocene catalyst from said aromatic
30 solvent;

 (i) washing said supported catalyst with a paraffinic hydrocarbon solvent at a reduced temperature of about 10°C or less; and

 (j) thereafter dispersing said supported metallocene in a viscous mineral oil having a viscosity substantially greater than the viscosity of said paraffinic hydrocarbon solvent.

24. The process of claim 23 wherein subsequent to step (h) and prior to step (i) washing the recovered supported metallocene catalyst with an aromatic solvent to remove unsupported metallocene from said supported metallocene catalyst and thereafter washing said supported catalyst in accordance with step (i).

25. The process of claim 23 wherein the weight ratio of said alumoxane to said silica is within the range of about 0.6-2.0.

26. The process of claim 23 wherein said stereospecific metallocene is a syndiospecific metallocene characterized by the formula:

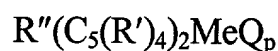


wherein Cp_a is a substituted cyclopentadienyl ring, Cp_b is an unsubstituted or substituted cyclopentadienyl ring; each R is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; each R'_m is the same or different and is a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the cyclopentadienyl rings imparting stereorigidity to the catalyst and is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal from the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; $0 \leq p \leq 3$; $0 \leq m \leq 4$; $1 \leq n \leq 4$; and wherein R'_m is selected such that $(Cp_bR'_m)$ is a sterically different ring than (Cp_aR_n) .

27. The process of claim 26 wherein the weight ratio of said alumoxane to said silica is within the range of about 0.6-2.0.

28. The process of claim 27 wherein the concentration of said metallocene on said support is within the range of 0.1-6 wt.%.

29. The method of claim 23 wherein said stereospecific metallocene is a chiral stereorigid metallocene characterized by the formula:



wherein each $(C_5(R')_4)$ is a substituted cyclopentadienyl ring; each R' is the same or different and is a hydrogen or hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the two $(C_5(R')_4)$ rings imparting stereorigidity to said catalyst with the two $(C_5(R')_4)$ rings being in a racemic configuration relative to Me, and R'' is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, a phosphorus hydrocarbyl radical, a nitrogen hydrocarbyl radical, a boron hydrocarbyl radical, and an aluminum hydrocarbyl radical; Me is a group 4b, 5b, or 6b metal as designated in the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; and $0 \leq p \leq 3$.

30. The process of claim 29 wherein the weight ratio of said alumoxane to said particulate silica support is within the range of about 0.6-2.0.

31. The process of claim 30 wherein the concentration of said metallocene on said support is within the range of 0.1-6.0 wt.%.